



Characterizing variable biogeochemical changes during the treatment of produced oilfield waste

Zacariah L. Hildenbrand^{a,b,*}, Inês C. Santos^{a,c,1}, Tiffany Liden^{a,c,1}, Doug D. Carlton Jr^{a,c,1}, Emmanuel Varona-Torres^{a,b,1}, Misty S. Martin^c, Michelle L. Reyes^c, Safwan R. Mulla^a, Kevin A. Schug^{a,c,**}

^a Affiliate of the Collaborative Laboratories for Environmental Analysis and Remediation, The University of Texas at Arlington, Arlington, TX 76019, United States

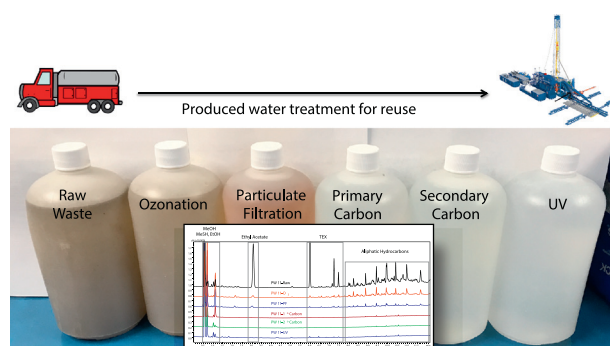
^b Inform Environmental, LLC, Dallas, TX 75206, United States

^c Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, TX 76019, United States

HIGHLIGHTS

- The biogeochemistry of waste from the Eagle Ford Shale was assessed.
- The efficacies of different water treatment technologies were evaluated.
- Resilient bacteria were found to survive different disinfection modalities.
- Multiple treatment processes are required for potential reuse.

GRAPHICAL ABSTRACT



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ABSTRACT

At the forefront of the discussions about climate change and energy independence has been the process of hydraulic fracturing, which utilizes large amounts of water, proppants, and chemical additives to stimulate sequestered hydrocarbons from impermeable subsurface strata. This process also produces large amounts of heterogeneous flowback and formation waters, the subsurface disposal of which has most recently been linked to the induction of anthropogenic earthquakes. As such, the management of these waste streams has provided a newfound impetus to explore recycling alternatives to reduce the reliance on subsurface disposal and fresh water resources. However, the biogeochemical characteristics of produced oilfield waste render its recycling and reutilization for production well stimulation a substantial challenge. Here we present a comprehensive analysis of produced waste from the Eagle Ford shale region before, during, and after treatment through adjustable separation, flocculation, and disinfection technologies. The collection of bulk measurements revealed significant reductions in suspended and dissolved constituents that could otherwise preclude untreated produced water from being utilized for production well stimulation. Additionally, a significant step-wise reduction in pertinent scaling and well-fouling elements was observed, in conjunction with notable fluctuations in the microbiomes of highly variable produced waters. Collectively, these data provide insight into the efficacies of available water

* Correspondence to Z.L. Hildenbrand, Inform Environmental, LLC, 6060 N. Central Expressway Suite 500, Dallas, TX 75206, United States.

** Correspondence to K.A. Schug, Department of Chemistry & Biochemistry, The University of Texas at Arlington, 700 Planetarium Pl., Box 19065, Arlington, TX 76019, United States.

E-mail addresses: zac@informenv.com, (Z.L. Hildenbrand), kschug@uta.edu. (K.A. Schug).

¹ Authors contributed equally.

treatment modalities within the shale energy sector, which is currently challenged with improving the environmental stewardship of produced water management.

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1. Introduction

The recycling of produced water and oilfield waste from unconventional oil and gas development (UD) has recently garnered significant attention given the scarcity of fresh water in many shale energy basins across the United States. For example, in 2011, 18.5 billion liters of water was used to stimulate unconventional production wells in Texas, which accounted for <1% of the state's water usage (Scanlon et al., 2014; Shaffer et al., 2013). However, these volumes tend to be highly localized, which can lead to ground water depletion, especially in arid and semiarid regions.

In addition to the requirement for large amounts of water, UD, as with conventional oil and gas development, also generates a tremendous amount of wastewater, commonly referred to as produced water (PW). This waste stream begins with flowback water (FBW: initial fracturing fluid returning to the surface), then transitions into produced water (a combination of formation water and fracturing fluid that is comingled with the oil and natural gas), which continues to be produced over the lifetime of a UD well (Liden et al., 2017). In 2012, oil and gas development in the United States generated an estimated 21.2 billion barrels (bbl) of produced water (58 million bbl/day), with Texas accounting for 35% of the national PW volume with >7.4 billion bbl (Veil, 2015).

Due to economics and convenience, subsurface injection has been the primary method of PW management in the United States, with up to 98% of PW being reinjected (Oetjen et al., 2017). Reinjection into a productive petroliferous formation can aide in oil recovery, whereas injection in a non-production formation can accomplish waste sequestration. However, the disposal of PW into salt-water disposal (SWD) wells has been linked to induced seismicity in some areas where the number of earthquakes correlates with the volume of PW being injected (Hornbach et al., 2016; Hornbach et al., 2015; van der Elst et al., 2015). It is thought that these anthropogenic events are the result of increased fluid pressure on already stressed faults, triggering preexisting faults to slip (Walsh and Zoback, 2015). As such, in addition to the inherent value of reducing the reliance on fresh water resources, particularly where water scarcity is an issue, the increased frequency of these UD-related earthquakes has provided motivation to reevaluate the viability of PW recycling for the sake of environmental stewardship.

If PW is to be recycled, then its biogeochemical characteristics require that a wide range of treatment technologies be utilized to remove the various biological, organic, and inorganic constituents that can otherwise preclude its reuse for production well stimulation and/or other beneficial uses, such as agriculture. For example, sulfate-reducing bacteria (SRB), iron-oxidizing bacteria (IOB), and acid-producing bacteria (APB), which can thrive under the extreme ionic and organic strengths of PW, can contribute to the costly degradation of product quality, referred to as souring, and the biocorrosion of metal infrastructure (AlAbbas et al., 2013; Murali Mohan et al., 2013). This corrosion of the production casing/tubing underground can potentially lead to casing failure and environmental contamination by petroleum products. Additionally, the presence of residual production and stimulation chemicals can limit the reuse of PW, particularly when there is the potential to negatively impact downhole stimulation chemistry (Liden et al., 2017). For example, if gel breakers remain in produced water, then the predetermined concentration of gellant and crosslinker will not be effective to achieve the necessary viscosity. Lastly, inorganic constituents can inhibit the potential reuse of PW for hydraulic fracturing due to scale formation and the potential for negative 'downhole' interactions. Formation water with a high level of pyrite, FeS₂, can oxidize

forming acidic conditions that can be corrosive to equipment (Chermak and Schreiber, 2014). The formation of the effective fracturing fluid can also be adversely impacted by free Fe, Ca, and Mg ions. Elevated levels of these and other multivalent cations compete with the added crosslinkers destabilizing the interactions and decreasing viscosity (Esmailirad et al., 2016). As such, the recycling of produced water cannot be optimized without a thorough understanding of the water composition in order to determine the treatment needs.

Here we present a comprehensive analysis of PW from the Eagle Ford shale region before, during, and after treatment through a multifaceted, modular water treatment system. A myriad of biological, organic, and inorganic variables were monitored in a step-wise fashion to assess the efficacy of tandem water treatment technologies within the context of reuse for UD. To the best of our knowledge, this is the first study where the biogeochemistry of produced water and its reusability have been comprehensively characterized following a diverse array of treatment modalities.

2. Materials and methods

2.1. Sample collection

Fourteen produced oilfield wastes with varying biogeochemical characteristics were acquired from numerous sources in the Eagle Ford Shale region as part of this study (Table 1). Irrespective of their subsurface origins, these wastes will be referred to as PW throughout the remainder of this text. Thirteen of the PW samples were collected for analysis before, during, and after treatment through a novel, multifaceted, modular recycling facility in Bebe, TX (Challenger Water Solutions, San Marcos, TX) (Fig. 1). Water quality was monitored in a step-wise fashion after an Ozonation (O₃) treatment, particulate filtration (PF), passage through primary and secondary carbon units (1° Carbon and 2° Carbon, respectively), and a UV treatment. Flushing of the treatment system was avoided in between individual waste streams to best emulate operational field conditions, with the exception of a single brine flush that was passed throughout the five different treatment modalities for routine maintenance. No chemical additives (i.e., coagulants

Table 1

Various oilfield wastes from the Eagle Ford Shale region that were analyzed before, during, and after treatment.

Sample ID	Sample notes
PW1	100 bbl of gel + breaker from waste pit. Only raw sample was collected as this fluid could not be run through water treatment system
PW2	Oilfield waste from gun barrel tanks of salt water disposal well site
PW2B	Oilfield waste from a second gun barrel tank from the same salt water disposal site as PW2
PW3	Oilfield waste from settling tanks of salt water disposal well site
PW3B	Oilfield waste from a second set of settling tanks from the same salt water disposal site as PW3
PW4	Oilfield waste from frac tanks of salt water disposal well site
PW4B	Oilfield waste from a second set of frac tanks from the same salt water disposal site as PW4
PW5	Flowback water
PW6	Produced water A
PW7	Produced water B (Gilette, TX)
PW8	Produced water C (Gonzales, TX)
PW9	Oilfield waste from waste water pipeline A
PW10	Oilfield waste from waste water pipeline B
PW11	Blend of PWs 8–10

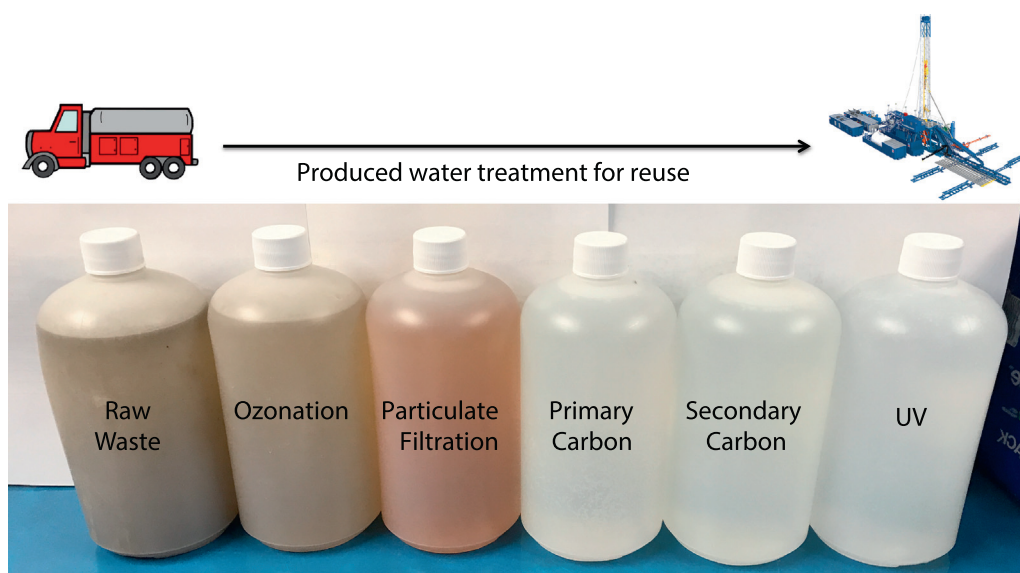


Fig. 1. Schematic illustrating the step-wise analysis of produced water throughout a multifaceted water recycling process.

and/or flocculants and/or biocides) were added at any time. All samples were collected under field conditions, where the recycling throughput was estimated to be approximately 15,000 bbl/day. All basic water quality measurements were collected onsite including those for temperature, dissolved oxygen (DO), conductivity, total dissolved solids (TDS), salinity, pH, turbidity, and oxidation-reduction potential (ORP) using a YSI Professional Plus multi-parametric probe. Samples for the microbial analysis were collected in duplicate in 500 mL HDPE sterile sample bottles (Thermo Scientific™ Nalgene™) by filling bottles completely and leaving minimal headspace. Samples for the analysis of organic constituents were collected in photo-resistant bottles without headspace. Samples for the analysis of inorganic constituents were preserved with nitric acid. Sterile deionized water was used as a transport blank to ensure that no contamination, either chemical or biological, occurred during the transportation of samples. Samples were stored on ice in coolers (4 °C) and then were refrigerated (4 °C) until analysis.

2.2. Microbial analysis

Microbial species were identified using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) and 16S ribosomal RNA (rRNA) sequencing, as described previously (Martin et al., 2018; Santos et al., 2017; Santos et al., 2018). Briefly, water samples were filtered within 24 h of collection using sterile membrane filters of 0.22 µm pore size (EMD Millipore). Membranes were plated onto Nutrient agar (NA), m-Endo Agar LES, and Aeromonas Isolation Agar (Sigma-Aldrich, St. Louis, MO, USA) and incubated at 25 °C (NA and Aeromonas Isolation agar) and 37 °C (m-Endo Agar) for 24–48 h. Bacterial quantification was performed and expressed as colony forming units (CFU)/mL according to Standard Methods for Water and Wastewater Analysis (APHA-AWWA-WPCF) (APHA-AWWA-WPCF, 1981).

Samples were prepared for MALDI-TOF MS analysis using the protein extraction method according to the instrument manufacturer guidelines (Shimadzu Corporation, Kyoto, Japan). MALDI-TOF MS (Kratos Analytical, Manchester, UK) experiments were performed by collecting and averaging 100 protein fingerprint spectra per spot, each a composite of 5 laser shots per spot, in a mass range of 2000–20,000 Da. *Escherichia coli* DH5α was used for calibration. The generated peak lists were automatically exported into the Shimadzu Axima Confidence plus SARAMIS microorganism database (BioMérieux, SA, Marcy l'Etoile, France), which provided identifications with

respective match scores. 16S rRNA gene sequencing was performed by the Genomics Core Facility (Department of Biology, UT Arlington, Arlington, TX) for confirmation of bacterial identification, in addition to the identification of bacteria with protein spectra not listed in the SARAMIS database (unknowns). A minimum of two independent PCRs was sequenced for each sample.

2.3. Analysis of organic constituents and TSS

The analysis of volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), total organic carbon, and total nitrogen was performed by headspace-gas chromatography (HS-GC), gas chromatography–mass spectrometry (GC–MS), and a TOC/TN analyzer, respectively (Carlton et al., 2017). Specific organic chemical species were selected from compounds identified in previous studies of contaminated groundwaters (Hildenbrand et al., 2015; Hildenbrand et al., 2016) and prior compositional analyses of produced oilfield waste (Thacker et al., 2015). Produced water was manually filtered through 13 mm PTFE syringe filters with 5 µm pores for TOC/TN analysis. Sample preparation for the HS-GC and GC–MS methods did not require filtration. Total suspended solids were quantified using gravimetric analysis. Produced water samples were filtered using Ahlstrom 1 µm Glass Microfiber Paper (Leominster, Ma) that were dried overnight at 90 °C.

2.4. Analysis of inorganic constituents and pertinent anions

A semi-quantitative analysis was completed using Shimadzu's ICPE-9000 (Columbia, Maryland) to determine the metals in solution and the relative concentrations during each step in the treatment sequence. Environmental Protection Agency method 200.7 was used to determine the concentration of select metals before and after treatment. Ion chromatography (IC) was used to quantify pertinent anions, as per EPA methods 300 and 310.1.

2.5. Statistical analyses

The non-parametric two-tailed Mann-Whitney *U* test was used to assess significant change between raw and treated PW samples. Additionally, the non-parametric Kruskal-Wallis one-way ANOVA was used to assess significant change amongst raw PW samples and those collected after the various treatment modalities. All statistical analyses were performed using the GraphPad Prism Software suite.

3. Results and discussion

3.1. Bulk measurements and pertinent anions

In addition to the basic water quality measurements that we performed on site, a series of bulk measurements were collected to assess the cumulative changes of organic, inorganic, and anionic constituents throughout the step-wise process. While bulk measurements do not specifically reveal the chemicals or ions in solution, they are quick measurements for the general state of the matrix of interest (Carlton et al., 2017). Turbidity and total suspended solids (TSS) are simple bulk measurements that can provide significant insight in the nature of the particulates in solutions. While the two are inherently related, the difference is a matter of particle size. Constituents in PW that can contribute to turbidity are generally $<1\ \mu\text{m}$ in size, such as dissolved solids, colloids, and bacteria; whereas particles $>1\ \mu\text{m}$ in size, such as oil droplets, formation sands, and proppants, contribute to the measurement of

TSS. Turbidity and TSS were both significantly reduced, from after ozonation through to after the UV treatment ($p = 0.0001$ and 0.012 , respectively), with overall average reductions from the raw sample values as great as 99.6% (Fig. 1A–B). The greatest stepwise reduction for turbidity was observed after the primary carbon unit (67.2%), whereas the particulate filter was responsible for the great stepwise reduction in TSS (97.4%). Currently there is no suggested guideline with respect to turbidity levels that are considered appropriate for reuse in production well stimulation; however, 500 mg/L has been suggested as an appropriate TSS cutoff for slick brine water fracs and gelled brine water fracs (King, 2011). Samples collected after particulate filtration, primary and secondary carbon, and UV treatment all exhibited average values below this reuse guideline (353.8, 167.0, 135.4, and 102.4, respectively) (Fig. 2B).

Total organic carbon and total nitrogen measurements also revealed significant step-wise reductions throughout the treatment process in 11 of the 13 raw PW samples ($p = 0.002$ and 0.008 , respectively) (Fig. 2C

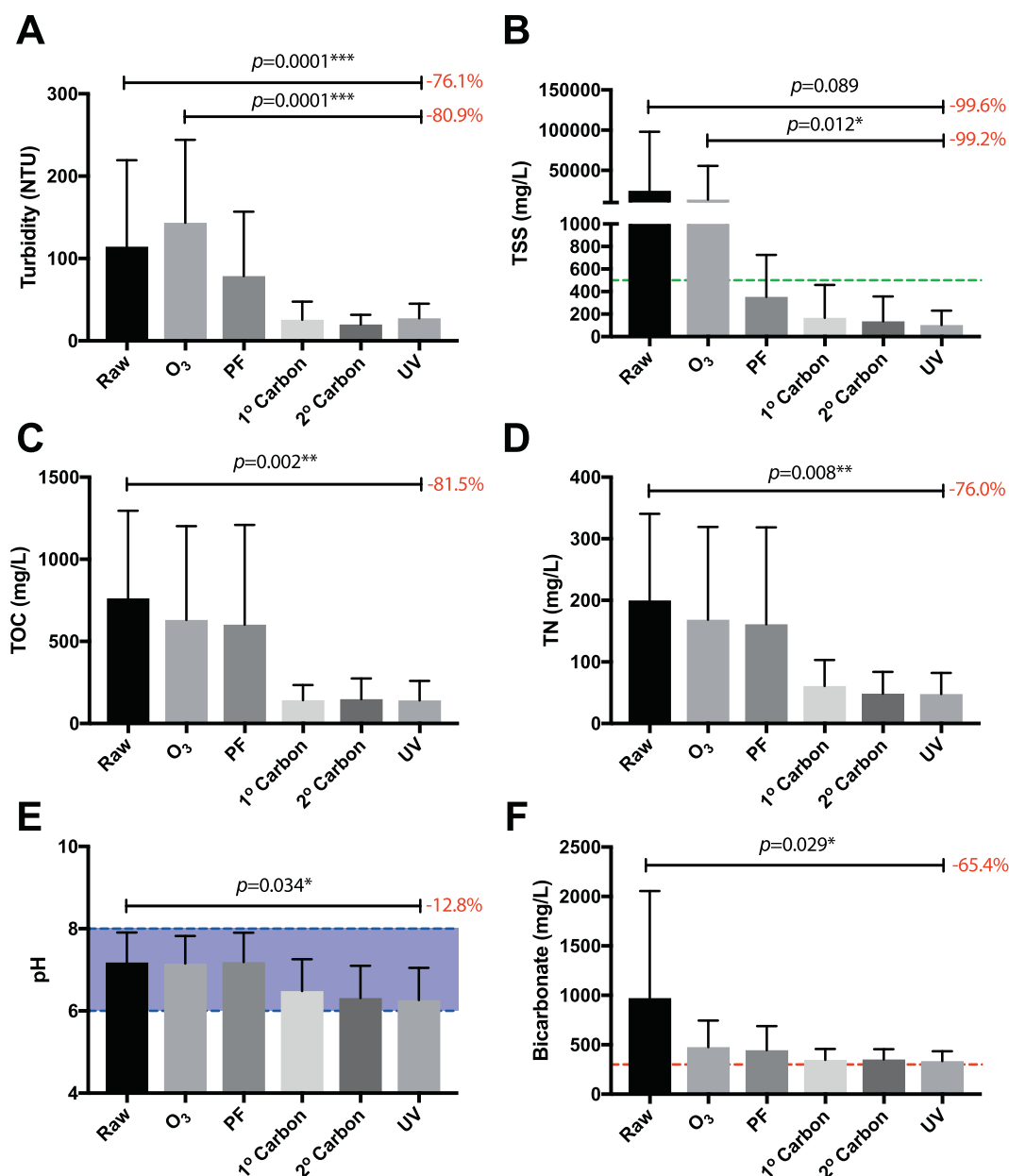


Fig. 2. The step-wise analysis of bulk measurements (A–D), pH (E), and bicarbonate (F). Green, blue, and red dashed lines represent recommended water quality guidelines for the reuse of produced water for production well stimulation made by King, Oetjen et al., and Tipton, respectively. Mean values graphed with error bars illustrating standard deviations. *, **, and *** denote p -values <0.05 , <0.01 , and <0.001 , respectively.

and D). Much like TSS, the greatest step-wise reductions resulted after passage through the primary carbon unit (76.4% for TOC and 62.3% for TN) with overall average reductions of 81.5% and 76.0%, respectively (Fig. 2C and D). It is also important to note that, prior to the analysis of total organic carbon, the collected samples were filtered through a polytetrafluoroethylene (PTFE) filter, which is an intrinsic requirement for this analysis, unlike the characterization of individual organic constituents via GC and GC-MS (Carlton et al., 2017). As such, it is possible that the hydrophobicity of PTFE resulted in a potential loss in total organic carbon signal (Calcagnile et al., 2012) for the samples preceding the primary carbon unit (raw, ozone, and particulate filtration), which may have ultimately contributed to some degree of under reporting with respect to the amount of total organic carbon removal following treatment. Nonetheless, there are no guidelines available for these bulk measurements within the context of reuse; however, elevated levels of TOC and TN can provide an optimal environment for the proliferation of undesirable bacterial communities (Santos et al., 2018).

pH is a basic water quality parameter that can be quite impactful on the success of production well stimulation when using fresh or recycled PW. A pH range between 6 and 8 is required to prevent clay hydration during hydraulic fracturing, which can negatively affect the permeability of the production strata, and ultimately, the extraction yield (Oetjen et al., 2017). All mean values fell within this range; however, pH levels decreased consistently throughout the treatment system, with an overall change of -12.8% from the raw sample values ($p = 0.034$) (Fig. 2E). This is interesting given that a shift in pH can counterbalance for elevated concentrations of bicarbonate, which can contribute to scaling and clay swelling within the reservoir (Collins, 1977; Waylisen and Fulton, 2012). Bicarbonate levels also exhibited a statistically significant 65.4% reduction throughout the system ($p = 0.029$), a majority of which occurred after ozonation (50.9% step-wise reduction following ozonation). Tipton suggested that 300 mg/L be considered a viable threshold for bicarbonate to determine whether or not PW is suitable for reuse (Fig. 2F) (Tipton, 2013). An equivalent threshold has been suggested for alkalinity (as carbonate) (Oetjen et al., 2017). The average value of bicarbonate exceeded this threshold (335 mg/L) upon passage through the five different treatment modalities; however, detectable levels of carbonate were only found in 2 out of the 63 collected samples (13.9 and 47.9 mg/L). Nonetheless, in addition to contributing to scale formation, alkalinity is a primary concern with respect to PW reuse as hard water can also cause fluid instability and affect pH (Waylisen and Fulton, 2012).

Total dissolved solids (TDS), a measurement that is primarily comprised of chloride, sulfate, and prominent metal ions such as sodium, can be a highly variable reflection of regional subsurface geochemistry for PWs. Concentrations can range from fresh water levels (<1000 mg/L) through saline (15,000–30,000 mg/L) to brine ($>300,000$ mg/L) levels (Otton and Mercier, 1995). In this study, TDS values ranged between 4700 and 40,100 mg/L for the 14 raw PW samples; however, TDS increased to as high as 127,000 and 135,000 mg/L in two samples acquired after the particulate filter (Fig. 3A). This notable increase was attributed to a brine flush that was performed as a form of general maintenance throughout the system. Despite this introduction of brine, TDS levels did not vary significantly across the various treatment modalities ($p = 0.959$). Chloride and sulfate concentrations exhibited similar patterns ($p = 0.976$ and 0.406), respectively, despite both displaying notable increases after the particulate filter (Fig. 3B and C). Elevated levels of TDS, in the form of chloride, do not preclude PW from reuse; in fact brines of varying weight are preferred under certain production well stimulation conditions. For example, 30,000–50,000 mg/L salinity (primarily chloride) is regarded as an optimal range for multiple brine-based fracturing scenarios (King, 2011). However, elevated levels of sulfate can inhibit the effectiveness of cross-linkers, which maintain viscosity in fracturing fluids (Esmailirad et al., 2016). Additionally, elevated levels of sulfate in injection water can react with barium and iron in the formation water

of a production well, and this can result in the precipitation of BaSO_4 and SrSO_4 scales (Hu et al., 2016). Sulfate also provides a substrate for SRBs that produce H_2S , which can alter the composition of hydrocarbon products and deteriorate production infrastructure (AlAbbas et al., 2013; Murali Mohan et al., 2013). Only one of the collected samples exceeded the 500 mg/L reuse threshold suggested by Oetjen et al. (639 mg/L); however, this post-particulate filter sample also displayed a chloride concentration of 117,000 mg/L, indicating that the two signals were both attributable to the brine flush.

Fluoride and bromide concentrations were also monitored in a step-wise fashion. Fluoride decreased 55.6% throughout the system, a majority of which resulted after passage through the primary carbon unit (45.9% reduction), albeit this compositional change was statistically insignificant ($p = 0.385$) due to the variability observed in the raw PW samples (<0.034 –62.9 mg/L) (Fig. 3D). To the best of our knowledge, there are no suggestive guidelines for fluoride levels in PW with respect to the stimulation of UD wells. However, under extreme geochemical conditions, fluoride can bind with calcium to form CaF_2 , which is regarded as an “exotic” scale that is even less soluble than BaSO_4 (Yuan et al., 2003). Bromide levels also did not significantly change across the system ($p = 0.942$). On average, a slight increase was observed when the raw samples were compared with the final UV-treated samples (75.4 vs. 104 mg/L, $p = 0.346$).

3.2. Bacterial communities

MALDI-TOF MS was used to monitor the microbial communities of produced water before, during, and after treatment. Table 2 illustrates the microbial composition of each raw PW and the composition throughout the treatment system. RNA sequencing was performed to identify bacteria that were not successfully identified using MALDI-TOF MS. The commercial MALDI-TOF MS microorganism database has been developed primarily for clinical applications, and thus can lack some entries for organisms that are more prevalent in the environment (Santos et al., 2016). As far as we know, this was the first time that this technique was used to identify the microorganisms present in produced water, as well as to help monitor the effectiveness of a produced water treatment unit. Mainly environmental bacteria were identified, which was expected since produced water was originally groundwater or surface water that was injected underground for oil and gas extraction. Most of the microorganisms identified are commonly found in soil and water, such as *Pseudomonas*, *Paracoccus*, *Aeromonas*, *Bacillus*, *Burkholderia*, *Rhizobium*, and others. Some uncommon microorganisms were also detected. For example, *Cronobacter sakazakii* is an opportunistic bacterium; however, its ecology is still unknown. Another, *Syncephalastrum racemosum*, is a fungus capable of degrading hydrocarbons in soil (Juhász and Naidu, 2000).

The identification of bacteria before treatment was performed to assess the type of microorganisms present in PW and to help determine the treatment effectiveness. Each raw produced water sample showed a very unique microbial population. We were unable to cultivate bacteria in one sample of raw PW (10), suggesting that the composition of this sample was so complex that the appropriate cultivation conditions, such as medium, temperature, oxygen percentage, and others, could not be established. It is important to note that some of the microorganisms that may be present could be unculturable and the only way to identify them would be by performing DNA sequencing. However, this technique, while effective, would not be able to distinguish between dead and viable cells, which is important when assessing disinfection efficiency. The raw PWs with cultivable bacteria displayed unique microbial profiles, which fluctuated greatly throughout treatment using the five different modalities (Table 2). There was notable variation in the bacterial removal efficacy between samples; with UV treatment being the most effective stepwise disinfection modality (28.5% decrease in total CFUs/mL). Surprisingly, total bacterial counts increased by 87.8% following ozonation, which is traditionally a very effective form of

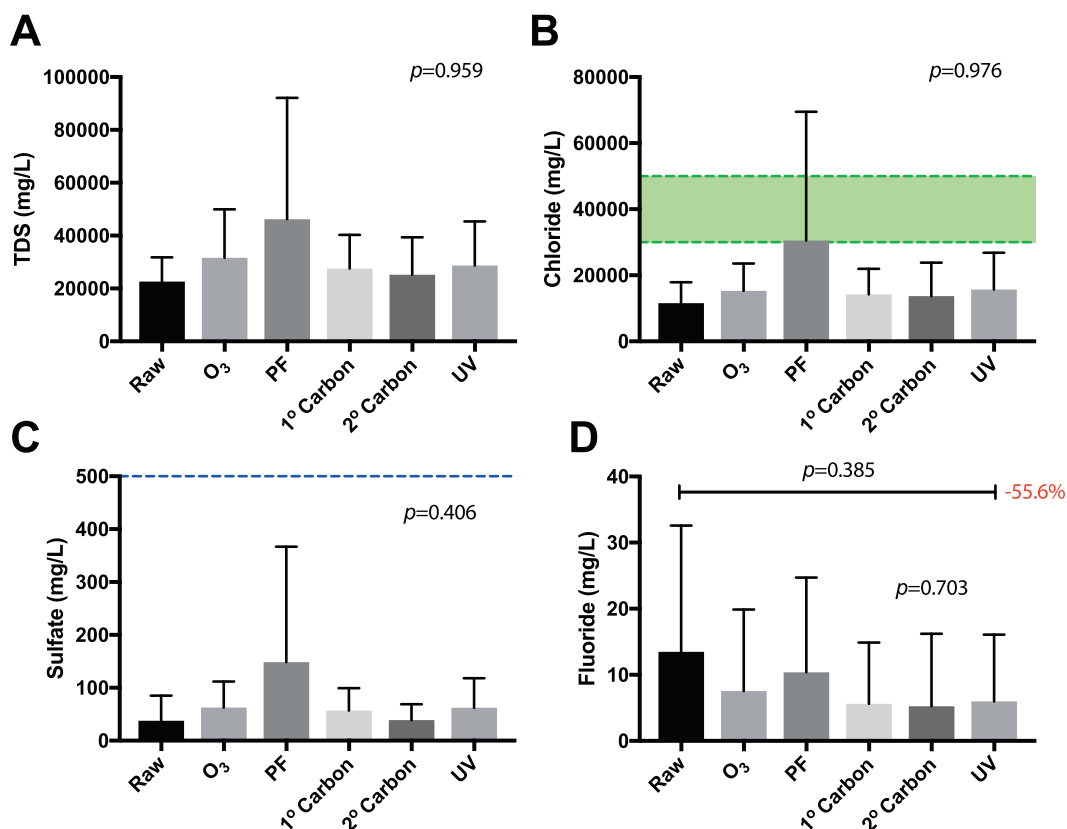


Fig. 3. The step-wise analysis of TDS (A), chloride (B), sulfate (C), and fluoride (D). Green and blue dashed lines represent recommended water quality guidelines for the reuse of produced water for production well stimulation made by King and Oetjen et al., respectively. Mean values are graphed with error bars illustrating standard deviations.

disinfection. However, low ORP values (-18.8 mV) revealed that collectively the ozonation treatment was not working effectively, as ORP values between 300 and 400 mV are generally regarded as the threshold for effective disinfection via ozonation. In fact, PWs 4 and 8 showed the presence of *Paracoccus* throughout the different modalities. Additionally, PW 6 was observed to contain *Pseudomonas* in all steps.

Interestingly, the levels of culturable bacteria, on average, displayed a 92.5% increase after passing through the primary carbon unit. We suspect that this increase was due to bacterial detachment from the carbon units after the water contacted these surfaces. Carbon units are an ideal environment for the growth of bacteria and biofilm formation. According to Kotlarz et al., passive biofilm detachment may occur continuously from surfaces by erosion or through discrete detachment events (Kotlarz et al., 2018). For this reason, the total removal of bacteria should be performed before the carbon units to avoid accumulation of microorganisms and formation of biofilms. The use of chemical additives could be an effective pretreatment option for the eradication of resilient bacteria. However, the widespread use of chlorine dioxide and other chaotrophic biocides can negatively impact production infrastructure. Nonetheless, if left untreated the presence of IOBs and SRBs in PW can limit its reuse, particularly for UD.

Pseudomonas aeruginosa was detected after complete treatment (PWs 3, 4, 6, and 7) and this microorganism can cause microbiologically induced corrosion (MIC) (Li et al., 2016b). Furthermore, *Shewanella* also plays a role in MIC as it is able to catalyze a variety of corrosion-promoting reactions (Dawood and Brozel, 1998). This microorganism was identified in the treated PW 10, and the use of this water in its current form could contribute to the degradation of product quality by the production of acid, and the biocorrosion of metal infrastructure. Microbially-induced corrosion of the production casing/tubing underground can potentially lead to casing failure and environmental contamination by petroleum products. Other anaerobic SRBs may have

also been present in the samples. However, the culmination of off site sampling, the transportation of the raw produced water samples, and laboratory growth conditions could only facilitate the cultivation of aerobic bacteria, facultative and aerotolerant anaerobes, and not obligate anaerobes. In the future, anoxic conditions will be used to account for the anaerobic fraction present in the samples. Such steps will require that the samples of raw PW be acquired directly from the production infrastructure.

The sequencing of unknown microorganisms identified multiple bacterial species that we had not observed in previous studies, including *Pannonibacter* sp., *Planococcus* sp., and *Pusillimonas* sp. *Planococcus* sp. is a halotolerant microorganism, meaning that it can tolerate the high levels of salt normally encountered in produced water (Table 2). *Pannonibacter* sp. is an alkali-tolerant microorganism capable of growing in alkaline environments at pH values >9.5 . As discussed before, high concentrations of bicarbonate ions were found in produced water. The alkalinity induced by the presence of bicarbonate ions provides a good environment for the growth of these type of bacteria. Additionally, *Pusillimonas* sp. has been previously found in diesel and other petroleum products. It is an oil-degrading bacterium (Cao et al., 2011), which may have a negative impact in oil production if its removal is not guaranteed. In summary, the assessment of the microbial content before, during, and after treatment is therefore extremely important to determine the best treatment modalities to use, the effectiveness of these modalities, and the type of field to which the treated water can be applied.

3.3. Organic constituents

Total organic carbon levels in the raw PWs were highly variable ranging from 217 to 1500 mg/L, which is consistent with previous analyses of PW from Texas (Maguire-Boyle and Barron, 2014; Thacker et al.,

Table 2

Bacteria detected by MALDI-TOF MS and rRNA sequencing. Percentages (%) correspond to relative matches in MALDI-TOF MS protein spectra to SARAMIS database. Identifications without % values were detected by rRNA sequencing, beyond the purview of the spectral database. Individual PWs are separated by color, whereas individual PW treatments and the bacterial species detected after each treatment are separated by bold and dashed lines, respectively.

Sample	Microorganism ID	CFUs/mL	Sample	Microorganism ID	CFUs/mL
PW1 Raw	<i>Aeromonas</i> sp. (83.8%) <i>Aeromonas</i> sp. (83.8%) <i>Aeromonas</i> sp. (83.8%)	>100	PW6 Raw	<i>P. aeruginosa</i> (99.9%) <i>P. aeruginosa</i> (99.9%) <i>P. aeruginosa</i> (99.9%) <i>P. aeruginosa</i> (99.9%)	5
	<i>Klebsiella</i> sp. <i>Klebsiella</i> sp. <i>Klebsiella</i> sp.	>4	PW6 O ₃ PW6 O ₃ PW6 O ₃ PW6 O ₃	<i>P. aeruginosa</i> (84%) <i>P. aeruginosa</i> (84%) <i>P. aeruginosa</i> (84%) <i>P. aeruginosa</i> (84%)	>2
	<i>Pseudomonas stutzeri</i>	>4	PW6 PF	—	—
	<i>Citrobacter</i> sp.	>100	PW6 PC	<i>P. aeruginosa</i> (84%) <i>P. aeruginosa</i> (84%) <i>P. aeruginosa</i> (84%) <i>P. aeruginosa</i> (84%)	420
PW2 Raw	<i>Pseudomonas</i> sp. <i>Pseudomonas</i> sp. <i>Pseudomonas</i> sp. <i>Pseudomonas</i> sp.	>100	PW6 SC	<i>Paracoccus</i> sp. (85.8%) <i>Paracoccus</i> sp. (85.8%) <i>Paracoccus</i> sp. (85.8%) <i>Paracoccus</i> sp. (85.8%)	5
	<i>Enterobacter</i> sp.	0.16		<i>P. aeruginosa</i> (96.5%) <i>P. aeruginosa</i> (96.5%) <i>P. aeruginosa</i> (96.5%) <i>P. aeruginosa</i> (96.5%)	5
				<i>B. cereus</i> group (86.7%) <i>B. cereus</i> group (86.7%) <i>B. cereus</i> group (86.7%) <i>B. cereus</i> group (86.7%)	5
				<i>A. baumannii</i> (80%) <i>A. baumannii</i> (80%) <i>A. baumannii</i> (80%) <i>A. baumannii</i> (80%)	5
PW2 O ₃ PW2 O ₃ PW2 O ₃ PW2 O ₃	<i>Pseudomonas</i> sp. <i>Pseudomonas</i> sp. <i>Pseudomonas</i> sp. <i>Pseudomonas</i> sp.	2	PW6 UV	<i>P. aeruginosa</i> (93.1%) <i>P. aeruginosa</i> (93.1%) <i>P. aeruginosa</i> (93.1%) <i>P. aeruginosa</i> (93.1%)	1.4
PW2 PF	<i>Bacillus</i> sp.	5	PW7 Raw	<i>Paracoccus</i> sp. (99.9%) <i>Paracoccus</i> sp. (99.9%) <i>Paracoccus</i> sp. (99.9%) <i>Paracoccus</i> sp. (99.9%)	2
PW2 PC	<i>Shewanella</i> sp. <i>Shewanella</i> sp. <i>Shewanella</i> sp. <i>Shewanella</i> sp.	0.2	PW7 O ₃ PW7 O ₃ PW7 O ₃ PW7 O ₃	<i>A. faecalis</i> (92.3%) <i>A. faecalis</i> (92.3%) <i>A. faecalis</i> (92.3%) <i>A. faecalis</i> (92.3%)	2000
	<i>Vibrio</i> sp. (fluvialis) <i>Vibrio</i> sp. (fluvialis) <i>Vibrio</i> sp. (fluvialis) <i>Vibrio</i> sp. (fluvialis)	>4		<i>Paracoccus</i> sp. (99.9%) <i>Paracoccus</i> sp. (99.9%) <i>Paracoccus</i> sp. (99.9%) <i>Paracoccus</i> sp. (99.9%)	1000
	<i>Aeromonas</i> sp. <i>Aeromonas</i> sp. <i>Aeromonas</i> sp. <i>Aeromonas</i> sp.	30		<i>C. hominis</i> (90%) <i>C. hominis</i> (90%) <i>C. hominis</i> (90%) <i>C. hominis</i> (90%)	8
	<i>P. aeruginosa</i> (79.8%)	>4		<i>Paracoccus</i> sp. (89.7%) <i>Paracoccus</i> sp. (89.7%) <i>Paracoccus</i> sp. (89.7%) <i>Paracoccus</i> sp. (89.7%)	1.2
PW2 UV	<i>Paracoccus</i> sp. (81.9%) <i>Paracoccus</i> sp. (81.9%) <i>Paracoccus</i> sp. (81.9%) <i>Paracoccus</i> sp. (81.9%)	100	PW7 PF	<i>Paracoccus</i> sp. (99.9%) <i>Paracoccus</i> sp. (99.9%) <i>Paracoccus</i> sp. (99.9%) <i>Paracoccus</i> sp. (99.9%)	8
PW3 PF	<i>Bacillus</i> sp. <i>Bacillus</i> sp. <i>Bacillus</i> sp. <i>Bacillus</i> sp.	10	PW7 PC	<i>Paracoccus</i> sp. (89.7%) <i>Paracoccus</i> sp. (89.7%) <i>Paracoccus</i> sp. (89.7%) <i>Paracoccus</i> sp. (89.7%)	1.2
PW3 PC	<i>A. pullulans</i> (79.5%)	4	PW7 SC	—	—
PW3 SC	<i>E. coli</i> (79.2%)	500	PW7 UV	<i>Pseudomonas</i> sp. <i>Pseudomonas</i> sp. <i>Pseudomonas</i> sp.	>10
	<i>Vibrio</i> sp. (fluvialis)	>4		<i>Alcaligenes faecalis</i>	15
	<i>P. aeruginosa</i>	1		<i>E. aurantiacum</i> (98.1%)	4
	<i>Citrobacter</i> sp.	>100		<i>A. baumannii</i> (77.4%)	1000
PW3 UV	<i>P. aeruginosa</i> (80.1%)	4	PW8 Raw	<i>A. punctata</i> (82.6%)	4
	<i>E. coli</i>	20		<i>S. epidermidis</i> (96.6%)	4
	<i>Aeromonas</i> sp.	5		<i>Planomicrobium</i> sp. (99.9%)	4
				<i>Pseudomonas</i> sp. (99.9%)	0.04
PW4 Raw	<i>Paracoccus</i> sp. (93.6%) <i>Paracoccus</i> sp. (93.6%) <i>Paracoccus</i> sp. (93.6%) <i>Paracoccus</i> sp. (93.6%)	0.04	PW8 O ₃ PW8 O ₃ PW8 O ₃ PW8 O ₃	<i>Paracoccus</i> sp. (99.9%)	4
	<i>Pseudomonas stutzeri</i> (75.4%) <i>Pseudomonas stutzeri</i> (75.4%) <i>Pseudomonas stutzeri</i> (75.4%) <i>Pseudomonas stutzeri</i> (75.4%)	0.08		<i>Pseudomonas</i> sp. (99.9%)	4
	<i>Staphylococcus epidermidis</i> (80%) <i>Staphylococcus epidermidis</i> (80%) <i>Staphylococcus epidermidis</i> (80%) <i>Staphylococcus epidermidis</i> (80%)	0.04		<i>Paracoccus</i> sp. (99.9%)	4
	<i>Microsporium gypseum</i> (79.9%) <i>Microsporium gypseum</i> (79.9%) <i>Microsporium gypseum</i> (79.9%) <i>Microsporium gypseum</i> (79.9%)	5		<i>Rhizobium</i> sp. (76.8%)	4
PW4 PF	<i>Campylobacter upsaliensis</i> (77%) <i>Campylobacter upsaliensis</i> (77%) <i>Campylobacter upsaliensis</i> (77%) <i>Campylobacter upsaliensis</i> (77%)	0.04	PW8 PF	<i>Paracoccus</i> sp. (93.6%)	4
	<i>Cronobacter sakazakii</i> (79.2%) <i>Cronobacter sakazakii</i> (79.2%) <i>Cronobacter sakazakii</i> (79.2%) <i>Cronobacter sakazakii</i> (79.2%)	0.04		<i>C. perfringens</i> (93.6%)	4
	<i>Microsporium canis</i> (84%) <i>Microsporium canis</i> (84%) <i>Microsporium canis</i> (84%) <i>Microsporium canis</i> (84%)	0.04		<i>R. ornitholytica</i> (82.9%)	4
	<i>Nocardia</i> sp. (76%) <i>Nocardia</i> sp. (76%) <i>Nocardia</i> sp. (76%) <i>Nocardia</i> sp. (76%)	0.04		<i>Paracoccus</i> sp. (89.7%)	4
PW4 O ₃ PW4 O ₃ PW4 O ₃ PW4 O ₃	<i>Paracoccus</i> sp. (99.9%) <i>Paracoccus</i> sp. (99.9%) <i>Paracoccus</i> sp. (99.9%) <i>Paracoccus</i> sp. (99.9%)	1	PW8 PC	<i>Pannonibacter</i> sp.	0.12
	<i>Staphylococcus ludgunensis</i> (78%) <i>Staphylococcus ludgunensis</i> (78%) <i>Staphylococcus ludgunensis</i> (78%) <i>Staphylococcus ludgunensis</i> (78%)	5		<i>S. putrefaciens</i> (75%)	500
	<i>Aspergillus flavus</i> (80%) <i>Aspergillus flavus</i> (80%) <i>Aspergillus flavus</i> (80%) <i>Aspergillus flavus</i> (80%)	5		<i>Paracoccus</i> sp. (81.9%)	40
	<i>Paracoccus</i> sp. (99.9%) <i>Paracoccus</i> sp. (99.9%) <i>Paracoccus</i> sp. (99.9%) <i>Paracoccus</i> sp. (99.9%)	0.04		<i>S. epidermidis</i> (99%)	40
PW4 PF	<i>Staphylococcus hominis</i> (85.5%) <i>Staphylococcus hominis</i> (85.5%) <i>Staphylococcus hominis</i> (85.5%) <i>Staphylococcus hominis</i> (85.5%)	0.04	PW8 UV	<i>S. putrefaciens</i> (99.9%)	0.16
	<i>Staphylococcus saprophyticus</i> (76.5%) <i>Staphylococcus saprophyticus</i> (76.5%) <i>Staphylococcus saprophyticus</i> (76.5%) <i>Staphylococcus saprophyticus</i> (76.5%)	0.04		<i>B. cereus</i> group (96.9%)	4
	<i>Penicillium chrysogenum</i> (79.8%) <i>Penicillium chrysogenum</i> (79.8%) <i>Penicillium chrysogenum</i> (79.8%) <i>Penicillium chrysogenum</i> (79.8%)	0.04		<i>Paracoccus</i> sp. (85.8%)	0.16
	<i>B. anthracis</i> (91.2%) <i>B. anthracis</i> (91.2%) <i>B. anthracis</i> (91.2%) <i>B. anthracis</i> (91.2%)	0.08	PW9 Raw	<i>S. hominis</i> (88.1%)	2
PW4 PC	<i>Prevotella bivia</i> (84%) <i>Prevotella bivia</i> (84%) <i>Prevotella bivia</i> (84%) <i>Prevotella bivia</i> (84%)	5		<i>S. maltophilia</i> (96%)	70
	<i>Microsporium gypseum</i> (89.3%) <i>Microsporium gypseum</i> (89.3%) <i>Microsporium gypseum</i> (89.3%) <i>Microsporium gypseum</i> (89.3%)	15		<i>Shewanella</i> sp.	10
	<i>Paracoccus</i> sp. (97.5%) <i>Paracoccus</i> sp. (97.5%) <i>Paracoccus</i> sp. (97.5%) <i>Paracoccus</i> sp. (97.5%)	40		<i>Alcaligenes faecalis</i>	70
PW4 SC	<i>Pseudomonas</i> sp. (75.6%) <i>Pseudomonas</i> sp. (75.6%) <i>Pseudomonas</i> sp. (75.6%) <i>Pseudomonas</i> sp. (75.6%)	5	PW9 O ₃ PW9 O ₃ PW9 O ₃ PW9 O ₃	<i>Pusillimonas</i> sp.	>100
	<i>Sphingomonas paucimobilis</i> (82.4%) <i>Sphingomonas paucimobilis</i> (82.4%) <i>Sphingomonas paucimobilis</i> (82.4%) <i>Sphingomonas paucimobilis</i> (82.4%)	>500		<i>B. cereus</i> group (87.4%)	4
	<i>Paracoccus</i> sp. (93.6%) <i>Paracoccus</i> sp. (93.6%) <i>Paracoccus</i> sp. (93.6%) <i>Paracoccus</i> sp. (93.6%)	60		<i>S. putrefaciens</i> (84.4%)	—
	<i>Burkholderia</i> sp. (99.9%) <i>Burkholderia</i> sp. (99.9%) <i>Burkholderia</i> sp. (99.9%) <i>Burkholderia</i> sp. (99.9%)	>500		<i>S. algae</i> (96.8%)	—
PW4 UV	<i>Bifidobacterium</i> sp. (79.9%) <i>Bifidobacterium</i> sp. (79.9%) <i>Bifidobacterium</i> sp. (79.9%) <i>Bifidobacterium</i> sp. (79.9%)	5	PW9 PC	<i>K. pneumoniae</i> (81.2%)	0.28
	<i>Aeromonas</i> sp. (77.7%)	>500		<i>P. chlororaphis</i> (76.1%)	1000
	<i>E. coli</i> (78.1%)	>250		<i>P. stutzeri</i>	—
	<i>Candida krusei</i> (84%)	5	PW9 SC	<i>Paracoccus</i> sp. (75%)	4
PW4 PF	<i>Pseudomonas</i> sp.	>100		<i>K. pneumoniae</i> (87%)	0.28
	<i>Burkholderia</i> sp. (84.5%)	>500		<i>B. stabilis</i> (87%)	0.2
	<i>Rhizomucor pusillus</i> (77.4%)	>500	PW9 UV	—	—
	<i>Pseudomonas</i> sp. (78.4%)	>500		<i>Planococcus</i> sp.	4
PW4 SC	<i>Exiguobacterium aurantiacum</i> (78.2%)	35		<i>Shewanella</i> sp.	20
	<i>E. coli</i> (86.5%)	>500		<i>B. cereus</i> group (96.9%)	8
PW4 UV	<i>Paracoccus</i> sp. (99.9%)	5	PW10 Raw	<i>S. putrefaciens</i> (80.6%)	0.8
	<i>B. anthracis</i> (76.8%)	1.2		<i>E. coli</i> (90.5%)	400
	<i>B. cereus</i> group (86.7%)	0.28		<i>Pseudomonas</i> sp. (99.9%)	20
	<i>Staphylococcus epidermidis</i> (75.6%)	75		<i>Paracoccus</i> sp. (97.5%)	8
PW5 Raw	<i>Paracoccus</i> sp. (78%)	5	PW10 PC	<i>H. alvei</i> (87.7%)	150
PW5 O ₃	<i>Bacillus</i> sp.	0.6		<i>Shewanella</i> sp.	20
PW5 PF	<i>P. aeruginosa</i> (93.4%)	10		<i>S. putrefaciens</i> (83.5%)	8
PW5 PC	<i>Bacillus</i> sp.	1		<i>Paracoccus</i> sp. (99.9%)	8
PW5 SC	<i>Staphylococcus epidermidis</i> (76.7%)	5	PW10 UV	<i>B. stabilis</i> (81.4%)	8
	<i>Paracoccus</i> sp. (78%)	0.4		<i>P. aeruginosa</i> (99.9%)	8
	<i>Syncephalastrum racemosum</i> (77.4%)	0.04		<i>A. faecalis</i> (88.4%)	4
	<i>Enterococcus gallinarum</i> (76%)	—	PW11 Raw	<i>E. coli</i> (87.5%)	4
PW5 UV	<i>Pseudomonas aeruginosa</i> (79.8%)	—		<i>A. niger</i> (77.5%)	1000
	—	—		<i>Paracoccus</i> sp. (99%)	2000
	—	—		<i>S. haemolyticus</i> (75.2%)	0.2
	—	—		<i>K. pneumoniae</i>	—
			PW11 O ₃	<i>Paracoccus</i> sp. (85.8%)	4
			PW11 PF		
			PW11 PC		
			PW11 SC		
			PW11 UV		

2015). Similarly, the composition of various volatile organic compounds varied greatly amongst the raw PWs with the detection of various alcohols, acetates, aromatic and aliphatic hydrocarbons, and microbial metabolites (Fig. 4). Methanol and ethanol were detected ubiquitously throughout the raw PWs, which collectively, within the context of UD, are utilized as surfactants, corrosion inhibitors, scale inhibitors, and biocides (Ground Water Protection Commission and Council and Interstate Oil and Gas Compact, 2018). Additional, n-propanol and n-butanol were detected in a total of five of the raw PW samples, where within the framework of UD, these alcohols can accompany zirconium- and boron-based crosslinkers (Ground Water Protection Commission and Council and Interstate Oil and Gas Compact, 2018). Ethyl acetate, an asphaltene and paraffin solvent, was also a prominent feature in the PWs, along with the BTEX (benzene, toluene, ethylbenzene and xylenes) class of hydrocarbon compounds.

As reflected by the significant reductions in total organic carbon values throughout the water treatment system, notable reductions in the frequency of detection and the concentrations of the detected organic constituents were observed in a step-wise fashion (Fig. 5). Through HS-GC analyses, the raw PWs exhibited a rich organic profile with between 54 and 96 different volatile species, whereas the treated samples displayed between 17 and 39 species, a significant reduction of 64.7% ($p < 0.0001$). More specifically, a 99.9% reduction in total alcohols (methanol, ethanol, n-propanol, and n-butanol), ethyl acetate, and total BTEX was achieved during treatment (Fig. 5). Additionally, the microbial metabolites dichloromethane and methanethiol experienced a 99.9 and 100.0% removal, respectively (Supplemental Dataset 1). Dichloromethane is of particular interest as it can be representative of the degradation of chlorinated solvents, and has been detected in contaminated groundwaters in the Barnett and Cline shale regions of Texas (Hildenbrand et al., 2015; Hildenbrand et al., 2016).

From a qualitative perspective, a majority of the organic constituents, such as BTEX (Supplemental Fig. 1) and C9–C30 aliphatic hydrocarbons (Supplemental Fig. 2), were removed upon passage through the primary carbon chamber. The detection of residual VOCs does not preclude treated PW from being utilized successfully for production well stimulation; however, it is also important to note that the GC analyses presented here do not cover all of the organic compounds that can be present in PW. For example, liquid chromatography-mass spectrometry (LC-MS) has been proven to be a powerful tool in the analysis of surfactants and polyethylene glycols (PEGs) commonly found in waste streams produced by UD (Thurman et al., 2014). LC-MS analyses would add value to subsequent PW reuse studies, particular if agricultural discharge is the terminal destination (Veil, 2015).

3.4. Target metal ions

As part of this study, an extensive analysis was performed to assess a wide range of prominent, and trace metal ions (Supplemental Dataset 1). Of particular interest within the context of PW reuse for production well stimulation are ions that can contribute to the formation of scale, as well as ions that can negatively impact crosslinker chemistry. Barium, calcium, magnesium, and strontium are generally the largest contributors to the formation scale (Hu et al., 2016), whereas elevated levels of boron, iron, titanium, and zirconium can lead to over crosslinking, reduced gel viscosity, altered temperature stability, and inefficient proppant dispersion (Waylisen and Fulton, 2012). Mean barium, calcium, and magnesium levels all increased upon passage through the five different treatment modalities, albeit these relative increases were not significant (p -values 0.35–0.71), and the resulting concentrations were below the respective reuse guidelines (Fig. 6). On the contrary, iron and strontium levels were both reduced upon treatment (p -values of 0.91 and 0.92, respectively), where the mean iron value following treatment exceeded the 10 mg/L threshold required for optimal crosslinker efficiency (17.6 mg/L), but not the suggested threshold for gelled brine water fracs of oil-bearing zones of 100 mg/L (King, 2011). Elevated boron levels were observed in a majority of the raw PW samples (50.2 mg/L), which is consistent with previous measurements of PW from the Eagle Ford region (Maguire-Boyle and Barron, 2014; Sari and Chellam, 2015). The treated samples also exceeded the suggested reuse value of 10 mg/L (49.5 mg/L) (Tipton, 2013), which is pertinent with respect to the use of boron-based crosslinkers, like sodium aminoboronate. However, titanium- and zirconium-based crosslinkers are also commonly used in UD (Li et al., 2016a), and these two ions were undetectable in any of the raw or treated samples.

With respect to changes in metal ion concentrations, a majority of the fluctuations occurred within the primary and secondary carbon units (Supplemental Dataset 1). This was best illustrated by dramatic variations in potassium and sodium levels, which are relatively inconsequential when assessing the viability of recycled PW. While the composition of the carbon-based treatment modalities in this study could not be disclosed for the sake of protecting proprietary trade secret information, it is not uncommon for there to be significant ion exchange when aqueous solutions enriched with barium, calcium, magnesium, potassium, sodium, and strontium interact with clay media (Hu et al., 2016). There may be room for improvement in terms of cation removal by exploring carbon materials that have high cation-exchange capacities, such as vermiculite and montmorillonite (Appelo and Postma, 2010). However, the effectiveness for precipitation and cation-

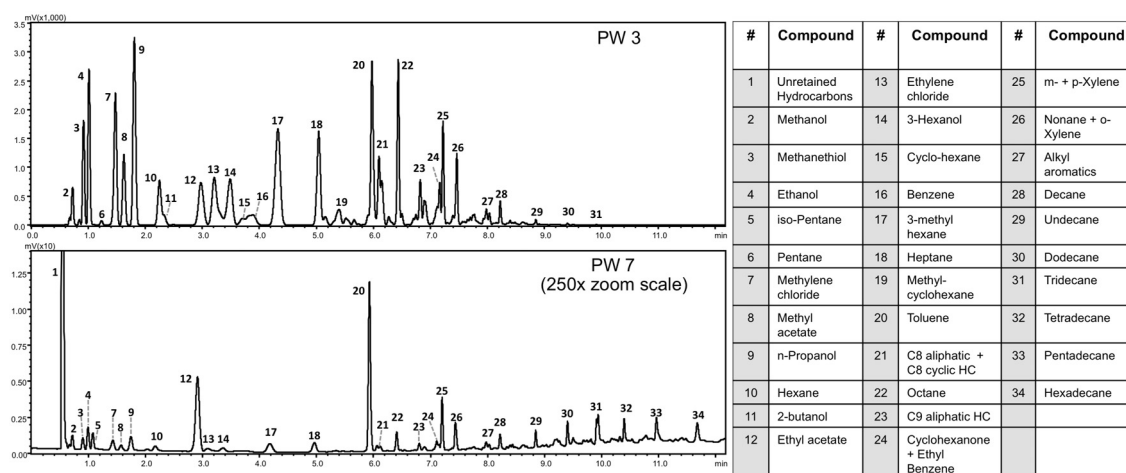


Fig. 4. The differentiation of individual organic species in raw produced water as visualized by GC analysis.

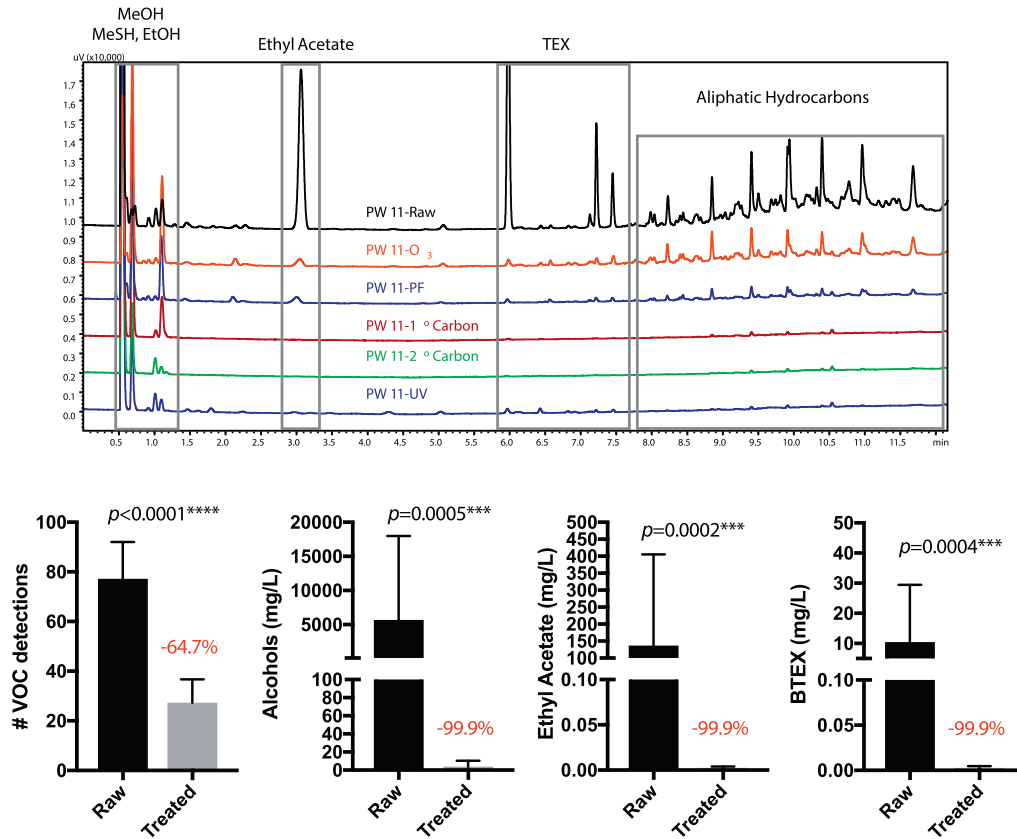


Fig. 5. (Top) The step-wise removal of prominent volatile organic compounds as visualized using gas chromatographic analysis. (Bottom) The reduction of organic species from raw PW following passage through all five treatment modalities (treated). Mean values graphed with error bars illustrating standard deviations. *, **, ***, and **** denote p -values < 0.05 , < 0.01 , < 0.001 , and < 0.0001 , respectively.

exchange with these material is generally dictated by the distribution of primary minerals (McCartney et al., 2012), which in the case of PW, can be highly variable.

Beyond the scope of reusing treated produced water for production well stimulation, it is important to remain cognizant of other metal ions that can dictate the success of subsequent treatment processes. For

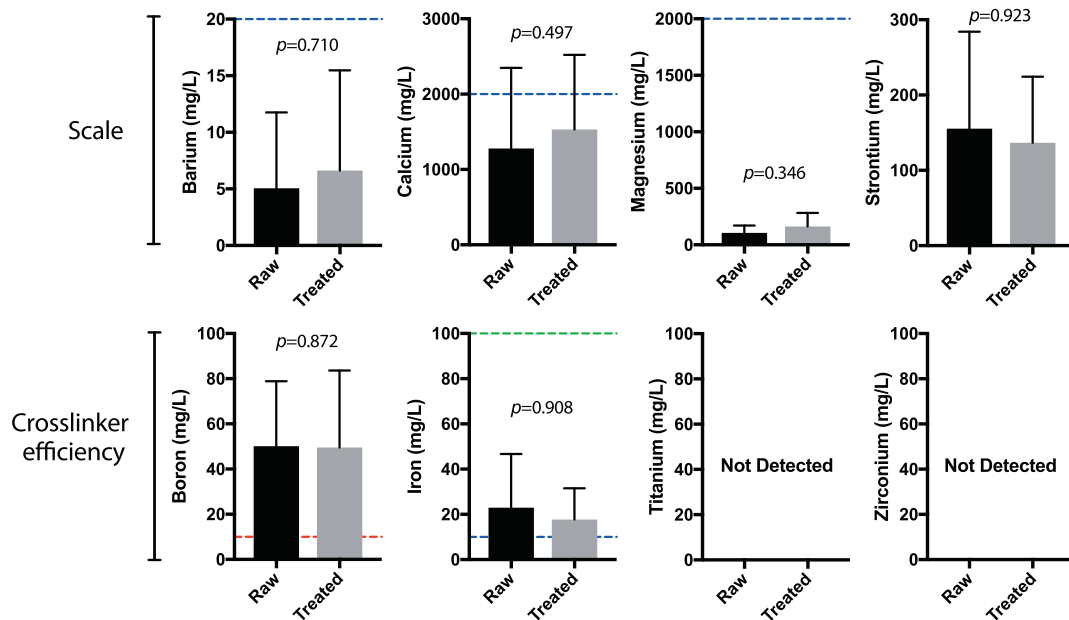


Fig. 6. Fluctuations of pertinent metals ions between raw and treated produced waters following passage through all five treatment modalities (treated), respectively. Green, blue, and red dashed lines represent recommended water quality guidelines for the reuse of produced water for production well stimulation made by King, Oetjen et al., and Tipton, respectively. Mean values graphed with error bars illustrating standard deviations.

example, if the terminal destination for treated produced water is agricultural discharge or even achieving a state of potability, then desalination is required to remove the elevated levels of salts, metals, and other trace elements. As such, one must consider natural constituents such as silica, which has been found to foul reverse osmosis (RO) membranes from exposure to brine solutions with concentrations between 130 and 160 mg/L (Malki and Abbas, 2013). The mean silica levels that were observed as part of this study were relatively low (37.2 and 25.5 mg/L for raw and treated samples, respectively); however, the elevated levels of TDS (maximum value of 52,280 mg/L) would preclude some of the treated samples from subsequent desalination via RO, and thus would require some form of distillation treatment.

4. Conclusion

Collectively, these findings are the result of a unique collaboration between scientists and engineers in an effort to comprehensively assess the reusability of produced oilfield waste from UD, for the sake of environmental stewardship. Shale energy extraction is a thirsty, multifaceted process that is heavily reliant on consistent, and ideally predictable chemistry, whereby a complete understanding of PW biogeochemistry is required prior to it being considered a viable resource for production well stimulation. As such, the exhaustive nature of the measurements presented here, to assess the treatment of highly variable industrial waste, clearly indicates that multiple treatment technologies are required in order to remove pertinent organic, inorganic, and biological contaminants below their respective reuse thresholds. The organic fraction of PW appears to be the easiest to remove, with a significant reduction in TOC and nearly complete elimination of prominent hydrocarbons and VOCs being accomplished by ozone-induced flocculation, particulate filtration, and passage through a primary carbon medium. However, the persistence of several multivalent metal ions throughout the different treatment modalities indicates that their removal may require ionically-rich PWs be treated with a range of clay matrices, which demonstrate high cation exchange capacities. In particular, the retention of elevated levels of boron and iron indicate that additional treatment modalities, beyond the scope of those evaluated in this study, are required for complete removal of these potentially disruptive ions. Lastly, these data identified a number of unique organophilic bacteria that exhibited resilience to traditional disinfection modalities. This phenomenon has recently been documented in chlorinated groundwater (Martin et al., 2018), albeit the precise mechanism and physiology for this survival under disinfection conditions remains to be determined.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.03.388>.

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Conflicts of interest

None.

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